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Synthesis, structure and optical limiting effect of two new nickel complexes containing strongly bound geometrically fixed multi-sulfur 1,2-dithiolene ligands showing remarkable near-IR absorption

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Two new nickel complexes containing strongly bound multi-sulfur 1,2-dithiolene ligands, $[NBu_4][Ni(bddt)_2]$ **1** and $[Ni(bddt)_2]$ **2** (bddt = 4a,5,6,7,8,8a-hexahydro-1,4-benzodithiin-2,3-dithiolate), have been synthesized and characterized by electrochemical measurements, IR and UV–VIS–NIR spectroscopies. The optical limiting properties of these nickel complexes have been determined with 32 ps laser pulses of 532 nm wavelength. The limiting thresholds of **1** and **2** are *ca.* 0.6 and 0.7 J cm^{-2}, respectively, which are comparable to that observed in C_{60}. Such results show that the nickel dithiolene complexes may be new candidates for optical limiting applications. In addition, the neutral complex $[Ni(bddt)_2]$ **2**, which shows remarkable absorption in the near-IR region ($\varepsilon = 63\,000$ dm^3 mol^{-1} cm^{-1} at 1035 nm) and is an excellent candidate as a near-IR dye for Q-switching neodymium lasers, has been additionally characterized by X-ray diffraction.

Introduction

Recently, optical limiting (OL) materials have been intensively studied owing to their potential applications in the protection of optical sensors and human eyes from high-intensity laser beams, based on various mechanisms including non-linear absorption and refraction and optical excited-state absorption. The most frequently reported materials are fullerenes (C_{60}),[1,2] phthalocyanine complexes[3,4] and some inorganic clusters.[5–10] A good optical limiter should have two characteristics: (1) large transmission at low intensities but low transmission at high intensities, (2) a low threshold for the onset of non-linear attenuation of the input beams. In addition, an ideal optical limiter should show a rapid response (picoseconds for some applications) and effectiveness over a wide wavelength range (*e.g.*, the visible spectrum).

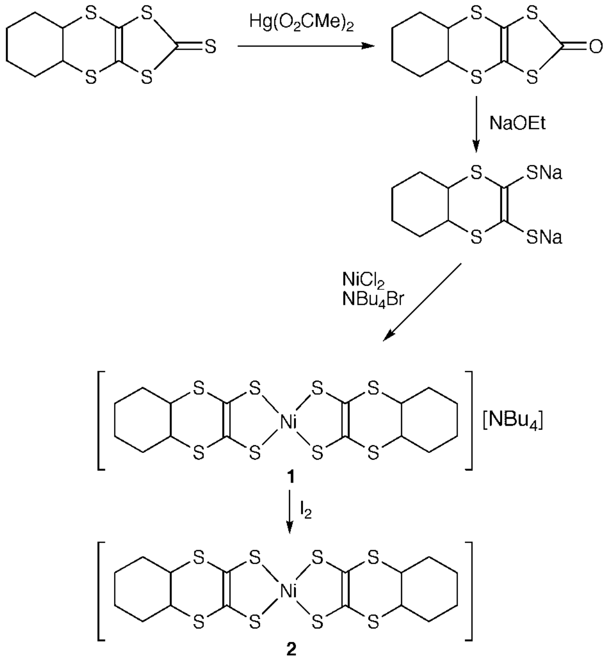
Nickel complexes of 1,2-dithiolene ligands are by no means new to materials chemistry and have been used as Q-switch dyes for near-IR (NIR) lasers such as Nd : YAG lasers since the early 1970s.[11–14] They have also been intensively studied as materials for molecular magnets, conductors and superconductors.[15–19] Recently, a number of complexes with third-order optical non-linearities were reported by us and others.[14,20–23] Here, we report the synthesis, characterization, structure and optical limiting effect of two new nickel complexes of a strongly coordinating multi-sulfur 1,2-dithiolene ligand. For the first time, the optical limiting behavior of nickel–dithiolenes has been investigated and results show that they have good response in the ps time scale.

Experimental

Scheme 1 summarizes the synthetic procedure leading to complexes $[NBu_4][Ni(bddt)_2]$ **1** and $[Ni(bddt)_2]$ **2** (bddt = 4a,5,6,7,8,8a-hexahydro-1,4-benzodithiin-2,3-dithiolate). 4,5-(*cis*-1,2-Cyclohexylenedithio)-1,3-dithiole-2-thione was prepared by the literature method.[24] All solvents were dried by standard techniques prior to use.

Syntheses

All reactions were carried out under N_2. Elemental analyses were performed using a Perkin-Elmer 240C analytical instrument. Ni analysis was performed on a Jarrell-Ash ICP.



Scheme 1

Preparation of 4,5-(*cis*-1,2-cyclohexylenedithio)-1,3-dithiole-2-one. 4,5-(*cis*-1,2-Cyclohexylenedithio)-1,3-dithiole-2-one was synthesized from 4,5-(*cis*-1,2-cyclohexylenedithio)-1,3-dithiole-2-thione. To the thione (1 g, 3.6 mmol) in chloroform (30 ml) glacial acetic acid (50 ml) was added mercury(II) acetate (4 g, 12.5 mmol). The mixture was stirred at room temperature for 6 h then filtered and the organic phase washed repeatedly with saturated sodium hydrogencarbonate and finally with water. Drying (sodium sulfate) and concentration *in vacuo* afforded yellow crystals. Recrystallization from ethanol gave good quality crystals. Yield: 0.66 g (70%); mp, 70–71 °C. (Calc. for $C_9H_{10}OS_4$: C, 41.22; H, 3.81. Found: C, 41.31; H, 3.80%). IR (KBr) ν/cm^{-1}: 1628 (C=O).

Preparation of [NBu$_4$][Ni(bddt)$_2$] 1. To a slurry of 4,5-(*cis*-1,2-cyclohexylenedithio)-1,3-dithiole-2-one (0.5 g, 1.9 mmol) in ethanol (20 ml), under N_2 atmosphere was added hexane-washed sodium (0.10 g, 4.3 mmol) and to the clear orange solution was added dropwise $NiCl_2\cdot 6H_2O$ (0.22 g, 0.9 mmol) in 20 ml ethanol. After 15 min, the solution was stirred in air for 30 min. The solution changed from amber to dark green as the reaction proceeded. After filtration, 1 equivalent of tetrabutylammonium bromide was added to the filtrate, and dark green solids were precipitated immediately. The green solids were collected by filtration and recrystallized from acetone. Yield: 0.40 g (54%) (Calc. for $C_{32}H_{56}NNiS_8$: C, 49.90; H, 7.28; N, 1.82; Ni, 7.63. Found: C, 50.06; H, 7.32; N, 1.80; Ni, 7.50%). IR (KBr) ν/cm^{-1}: 2920w, 1455s, 1188s, 855m, 402s, 362w. Raman ν/cm^{-1}: 447m, 363s, 123w.

Preparation of [Ni(bddt$_2$] 2. The neutral complex **2** obtained as a black powder was prepared by I_2-oxidation of complex **1**. Black block crystals were obtained upon recrystallization from carbon disulfide. (Calc. for $C_{16}H_{20}NiS_8$: C, 36.40; H, 4.17; Ni, 11.12. Found: C, 36.30; H, 4.21; Ni, 11.25%). IR (KBr) ν/cm^{-1}: 2919w, 1237s, 1180s, 889m, 414s, 360w. Raman ν/cm^{-1}: 458m, 369s, 126w.

Physical measurements

IR spectra were recorded on a Nicolet FTIR 170SX spectrophotometer. FT-Raman spectra (in the range 500–100 cm^{-1} and in the solid state) were recorded on a Bruker RFS100 FT-Raman spectrometer. UV–VIS spectra were recorded on a UV-3100 spectrophotometer. Cyclic voltammetry was performed using a model 79-1 V-A analyser with an electrochemical cell using a platinum wire as the working electrode, a platinum plate as the auxiliary electrode and an SCE as the reference electrode. Nitrogen was passed through the solution in the cell for 15 min prior to each measurement.

Structure determination

A black block crystal of [Ni(bddt)$_2$] **2** with approximate dimensions 0.46 × 0.24 × 0.22 mm was mounted in air. The intensity data were collected at 293(2) K on a Siemens SMART CCD diffractometer with a detector distance of 4 cm and frame exposure time of 30 s. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using SHELXTL software,[25] with 1706 unique absorption corrected (empirical, $T_{\min} = 0.633$, $T_{\max} = 0.789$) reflections. All non-hydrogen atoms were anisotropically refined. The refinement converged at $R = 0.0211$ and $wR = 0.0510$ for a total of 155 parameters and 1706 observed reflections with $[I > 2.0\sigma(I)]$. Table 1 lists the crystallographic data.

Table 1 Crystal data and structure refinement for [Ni(bddt)$_2$] **2**

Chemical formula	$C_{16}H_{20}NiS_8$
Formula weight	527.51
Crystal system	Monoclinic
Space group	$P2_1/n$
μ/mm^{-1}	1.796
Unit cell dimensions	
a/Å	12.171(2)
b/Å	5.2299(7)
c/Å	16.567(2)
β/°	107.709(10)
V/Å^3	1004.6(2)
T/K	293(2)
Measured/independent reflections (R_{int})	5078/1706 (0.0172)
R	0.0211

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters for [Ni(bddt)$_2$] **2**. U_{eq} is defined as one third of the orthogonalized U_{ij} tensor

	x	y	z	10^3 U_{eq}/Å^2
Ni	0	0	0	31(1)
S(1)	1618(1)	408(1)	−235(1)	36(1)
S(2)	700(1)	−2724(1)	973(1)	38(1)
S(3)	3907(1)	−1732(1)	365(1)	38(1)
S(4)	2865(1)	−5415(1)	1709(1)	37(1)
C(1)	2512(2)	−1705(4)	442(1)	28(1)
C(2)	2102(2)	−3119(3)	997(1)	29(1)
C(3)	4696(2)	−4197(4)	1101(1)	30(1)
C(4)	4351(2)	−4387(4)	1906(1)	28(1)
C(5)	4649(2)	−2012(4)	2460(1)	34(1)
C(6)	5933(2)	−1387(5)	2668(2)	41(1)
C(7)	6307(2)	−1164(4)	1878(2)	40(1)
C(8)	5979(2)	−3505(4)	1310(1)	34(1)

Table 3 Bond lengths (Å) and angles (°) for [Ni(bddt)$_2$] **2**[a]

Ni–S(2)	2.1260(5)	Ni–S(2A)	2.1260(5)
Ni–S(1A)	2.1317(6)	Ni–S(1)	2.1317(6)
S(1)–C(1)	1.709(2)	S(2)–C(2)	1.707(2)
S(3)–C(1)	1.740(2)	S(3)–C(3)	1.833(2)
S(4)–C(2)	1.741(2)	S(4)–C(4)	1.819(2)
C(1)–C(2)	1.388(3)	C(3)–C(4)	1.518(3)
C(3)–C(8)	1.535(3)	C(4)–C(5)	1.521(3)
C(5)–C(6)	1.529(3)	C(6)–C(7)	1.516(3)
C(7)–C(8)	1.522(3)		
S(2)–Ni-S(2A)	180.0	S(2)–Ni–S(1A)	88.47(2)
S(2A)–Ni–S(1A)	91.53(2)	S(2)–Ni–S(1)	91.53(2)
S(2A)–Ni–S(1)	88.47(2)	S(1A)–Ni–S(1)	180.0
C(1)–S(1)–Ni	104.75(7)	C(2)–S(2)–Ni	105.40(7)
C(1)–S(3)–C(3)	106.43(9)	C(2)–S(4)–C(4)	102.39(9)
C(2)–C(1)–S(1)	119.59(14)	C(2)–C(1)–S(3)	126.9(2)
S(1)–C(1)–S(3)	113.46(11)	C(1)–C(2)–S(2)	118.67(14)
C(1)–C(2)–S(4)	126.2(2)	S(2)–C(2)–S(4)	115.04(11)
C(4)–C(3)–C(8)	110.6(2)	C(4)–C(3)–S(3)	113.66(13)
C(8)–C(3)–S(3)	105.95(14)	C(3)–C(4)–C(5)	113.4(2)
C(3)–C(4)–S(4)	112.78(13)	C(5)–C(4)–S(4)	113.04(13)
C(4)–C(5)–C(6)	110.5(2)	C(7)–C(6)–C(5)	112.1(2)
C(6)–C(7)-C(8)	112.7(2)		

[a] Atoms labeled A are related by an inversion center.

Atomic coordinates for all the non-hydrogen atoms are listed in Table 2, and selected atomic distances and bond angles are listed in Table 3. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, 1999, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/167.

See http://www.rsc.org/suppdata/jm/1999/2419/ for crystallographic files in .cif format.

Results and discussion

Preparation, IR and cyclic voltammetry

In the course of preparation of complex **1** , we directly used the product of hydrolysis of 4,5-(*cis*-1,2-cyclohexylenedithio)-1,3-dithiole-2-one without separation of the disodium salt, Na_2bddt, since the disodium salt is extremely sensitive to air.

$[NBu_4][Ni(bddt)_2]$ **1** displays a very rich IR spectrum with characteristic absorptions of monoanionic nickel dithiolenes,[26] ν_1 (C=C) at 1455 cm^{-1}; ν_2 (C=S) at 1188 cm^{-1}; ν_3 R–C$\genfrac{}{}{0pt}{}{S}{C}$ at 855 cm^{-1}; ν_4 and ν_5 (Ni–S) at 402 and 362 cm^{-1}, while the neutral complex **2** shows these absorptions at 1237, 1180, 880, 414 and 360 cm^{-1}, respectively.

The electrochemistry of complex **1** was investigated using cyclic voltammetry in CH_2Cl_2 (0.4 mol dm^{-3} NBu_4ClO_4, 0.1 V s^{-1}) (Fig. 1). The voltammogram shows the presence of three redox couples in the recorded region. The first one-electron reduction assigned to $[Ni(bddt)_2]^{2-}$–$[Ni(bddt)_2]^-$ is irreversible which is in contrast with other nickel–dithiolene complexes,[16,27] and may be due to the high scan rate used.[12,13] The second reversible peak is assigned to $[Ni(bddt)_2]^-$–$[Ni(bddt)_2]$. A third quasi-reversible peak is also observed at more positive potential ($E_{1/2} = 0.907$ V) which can be reasonably assigned to oxidation of the ligand.[12b,16]

Crystal structure of complex 2

The X-ray crystal structure determination of complex **2** (Fig. 2) shows that the Ni atom is coordinated in a square planar geometry with the two vicinal exocyclic sulfur atoms of the two chetating ligands. The Ni atom lies at an inversion center and hence both halves of the molecule are identical. The five-membered rings are virtually planar with a maximum deviation of 0.049(2) Å for C(1). The six-membered ring defined by C(1), C(2), C(3), C(4), S(3) and S(4) and its symmetry counterpart adopts a sofa conformation with C(4) deviating from the mean plane formed by the remainder of the atoms in that ring by −0.733(2) Å. The cyclohexyl rings adopt a chair conformation preventing the formation of stacks with short intermolecular contacts. Molecules translated one unit cell along the *b* direction are stacked at a perpendicular distance of 3.830 Å (Fig. 3). The closest intermolecular S⋯S contact is 3.8052(9) Å. Bond distances and angles in the NiS_4C_4 framework are similar to those reported for other neutral nickel dithiolenes.[12,14]

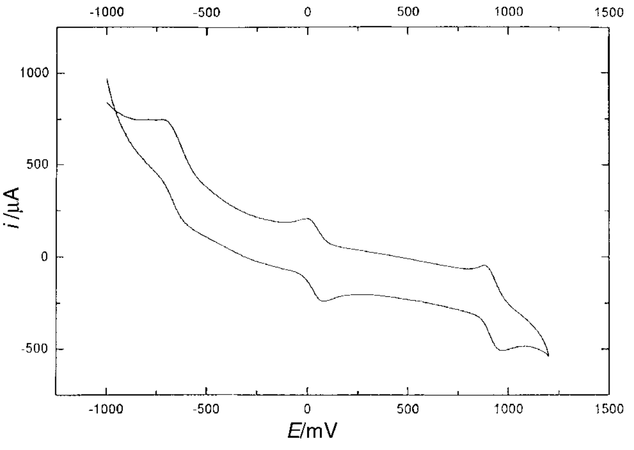


Fig. 1 Cyclic voltammogram of $[NBu_4][Ni(bddt)_2]$ **1** (3.1×10^{-4} mol dm^{-3}) in CH_2Cl_2–NBu_4ClO_4 (0.4 mol dm^{-3}) at a Pt electrode with a scan rate of 0.1 V s^{-1} .

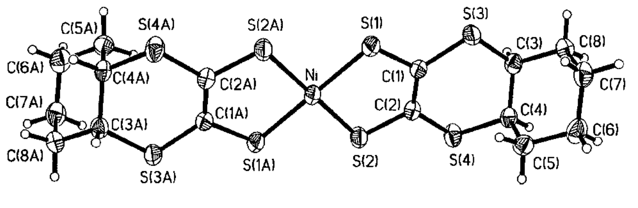


Fig. 2 Molecular structure and atom labeling scheme of $[Ni(bddt)_2]$ **2**.

UV–VIS–NIR spectra

The UV–VIS–NIR spectra of the complexes **1** and **2** are shown in Fig. 4. Complex **1** in acetonitrile solution shows a strong broad absorption at 1180 nm ($\varepsilon = 16\,800$ dm^3 mol^{-1} cm^{-1}), which is assigned to a π–π* transition ($2b_{1u} \rightarrow 3b_{2g}$).[11] The characteristic long-wavelength transition is found in the complex **2** at 1035 nm and shows an intensity ($\varepsilon = 63\,000$ dm^3 mol^{-1} cm^{-1}) much higher than those reported for previous nickel–dithiolene complexes,[11] even for similar complexes containing SR donors.[14,28] Complex **2** is thought to show such a strong intensity owing to the strongly coordinated ideally positioned donors in the ligands. This phenomenon confirms the conclusion that such ideally fixed donor groups increase the absorption coefficient substantially.[11]

In comparison with complex $[Ni(Pr^i_2timdt)_2]$[12,13] (Pr^i_2-timdt = 1,3-diisopropylimidazoline-2,4,5-trithione) having highest intensity at 1002 cm^{-1} ($\varepsilon = 80\,000$ dm^3 mol^{-1} cm^{-1}), the transition in this complex is much nearer to 1060 nm at which Q-switching neodymium lasers operate, hence this complex is an excellent candidate as a near-IR dye for Q-switching neodymium lasers.

It should be noted that the two compounds have relatively low linear absorptivity at 532 nm. This result is important since an ideal optical limiter should be transparent at low fluences.

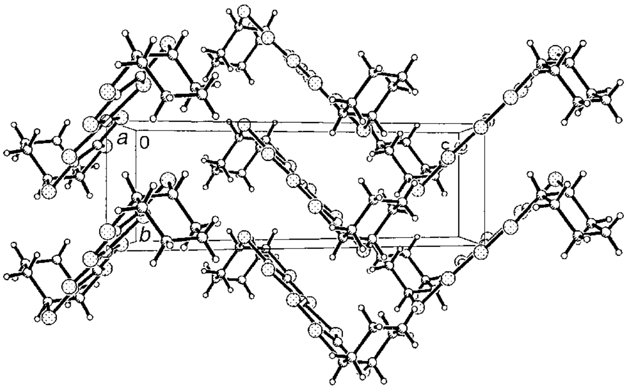


Fig. 3 Packing of the molecules in the unit cell of $[Ni(bddt)_2]$ **2** viewed down the *a* axis.

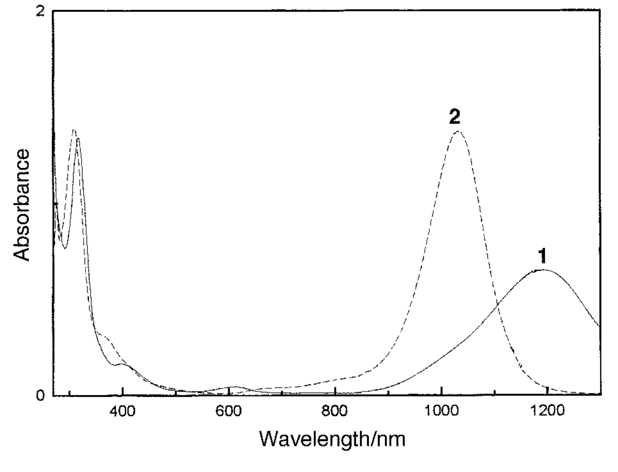


Fig. 4 UV–VIS–NIR spectra of complexes **1** (3.93×10^{-5} M) and **2** (2.18×10^{-5} M) in C_6H_6 solution. The optical pathlength is 1 cm.

Optical limiting properties

The optical limiting properties of complexes **1** and **2** were investigated. A benzene solution of the complex was placed in a 1 mm thick quartz cell and the sample irradiated by a frequency-doubled, Q-switched, mode-locked Nd : YAG laser, which produced linearly polarized 35 ps (FWHM) optical pulses at 532 nm with a repetition rate of 10 Hz. The spatial profiles of the optical pulses were nearly Gaussian after passing through a spatial filter. The pulses were split into two parts: the reflected pulse was used as reference, while the transmitted pulse was focused onto the sample by using a focusing mirror of 25 cm focal length. The sample was placed at the focus where the spot radius of the pulses was 28 ± 2 μm, as measured by the Z-scan technique.[28] Both the incident and transmitted laser pulses were monitored simultaneously by using two energy detectors (Rjp-735 energy probes, Laser Precision).

The optical limiting phenomenon was observed by measuring the non-linear (energy-dependent) transmission. An aperture was placed in front of the transmission detector when the measurements were performed. In our experiments, the maximum incident fluence at the sample was set at 4 J cm^{-2}. The optical limiting responses of benzene solutions of complexes **1** and **2** are depicted in Fig. 5. At very low input fluences, the optical responses of the two solutions behave linearly. As the incident fluence reaches *ca.* 0.3 J cm^{-2}, the transmittance begins to decrease rapidly. We define the limiting threshold as the incident fluence at which the transmittance falls to 50% of the linear transmittance. From Fig. 5, we determine the limiting thresholds of complexes **1** and **2** to be *ca.* 6 and 0.7 J cm^{-2}, respectively. The limiting thresholds of the two complexes are comparable with each other and also to that of C_{60} in toluene solution.[2]

It should be pointed out that our measurements of the transmitted pulse energy were conducted with the aperture placed in front of the transmission detector. Therefore, the observed optical limiting behavior for the complexes can be attributed to both non-linear absorptive and refractive processes.

The idea behind our choice of exploring these nickel dithiolenes as very promising candidates for OL applications is based on several important properties including the low limiting thresholds comparable to that of C_{60} in toluene solution. In addition, (1) compounds **1** and **2** have ultrafast response times owing to their highly delocalized π systems. They are amongst only a few materials which have good optical limiting effects for ps lasers such as C_{60} and the inorganic cluster $[(\eta\text{-}C_5H_5)CoFe_2SSe(CO)_6]$.[2,9] (2) They have broad spectral responses; in the spectral region 400–900 nm these compounds are essentially transparent. In this context they are superior to phthalocyanine derivatives which are narrow-band limiters. (3) They exist in well defined oxidation states, neutral and monoanionic; hence it is possible to control the oxidation states to optimize optical limiting effects. (4) They are also known to be very stable to intense irradition and hence suitable macroscopic systems may be prepared for practical application, such as solid host media and LB films.[23] In terms of these advantages, compounds **1** and **2** are superior to some inorganic clusters and other optical limiting materials.[5]

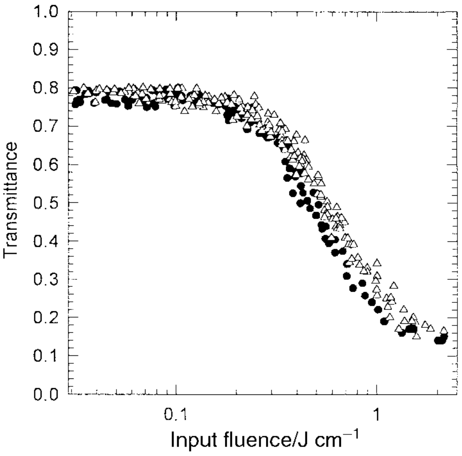


Fig. 5 Optical limiting response to 35 ps, 532 nm laser pulses. The energy transmittance is plotted *vs.* the incident fluence for complexes **1** [6.8×10^{-5} M (●)] and **2** [2.7×10^{-5} M (△)] in benzene solution. The optical pathlength is 1 mm.

Summary

Two new nickel dithiolene complexes have been synthesized and characterized and the optical limiting behaviour of nickel dithiolenes have been investigated for the first time. Compared with most successful optical limiting materials such as C_{60}, phthalocyanines and some inorganic clusters, they appear to be excellent candidates for optical limiting of ps lasers in the visible spectrum. In addition the structure of the neutral complex $[Ni(bddt)_2]$ **2** was determined by X-ray diffraction. Complex **2** shows remarkable absorption in the near-IR region and is an excellent candidate as a near-IR dye for Q-switching neodymium lasers.

Acknowledgements

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